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## PATENT SPECIFICATION



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### PROVISIONAL SPECIFICATION

#### Improvements in the Treatment of Chrome Tanned Leather

We, JOHN BURCHILL, HENRY ALFRED PIGGOTT, and GEORGE STUART JAMES WHITE, all of Hexagon House, Blackley, Manchester, all British Subjects, and  
5 IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention to  
10 be as follows:—

Chrome tanned leather when once dried is difficult or impossible to wet back satisfactorily for dyeing purposes by simple immersion in water, whether or not  
15 accompanied by mechanical assistance such as is obtained by drumming.

Various proposals have been made for overcoming this difficulty, for instance, the chrome tanned leather, previous to  
20 drying, is treated with an aqueous solution of an aromatic sulphonic acid or its salts or of a monoacylated or unsymmetrically diacylated diamine or, previous to drying, the leather is treated with a strong  
25 aqueous solution of a highly soluble inorganic salt such as magnesium chloride or the leather, previous to drying, is dehydrated by treatment with acetone.

However effective any one of these processes may be, they suffer from certain disadvantages. Thus when treated with an organic base or sulphonic acid as above described, the affinity of the leather for  
30 dyestuffs as compared with non-treated (undried) leather, is altered so that the leather dyer is liable to obtain on such leather with a given dyestuff results different from those to which he is accustomed; in the case of treatment with  
40 solutions of inorganic salts the salts on drying and storage may sweat out, forming undesired incrustations and crystallising within the pores of the leather, thus subjecting it to injurious stresses  
45 and causing shrinkage. The acetone method necessitates the use of an expensive organic solvent and a special plant is necessary for its economical recovery.

50 We have discovered a process whereby direct chrome tanned leather may be wetted back readily and at the same time the above enumerated disadvantages

avoided.

Our process consists in treating the  
55 chrome tanned leather, previous to drying, with an aqueous solution of a neutral polyhydroxy compound containing at least one ether group or a polyether compound  
60 which may or may not contain free hydroxyl groups. These compounds are characterised by high water solubility.

As examples of such we mention condensation products of carbohydrates, particularly the sugars, with ethylene oxide,  
65 polyethylene oxide itself (cf. Specification No. 346,550), the polyglycerols, condensation products of substances containing hydroxy or amino groups with ethylene oxide, for example polyethenoxyurea (cf.  
70 Specification No. 432,356) or polyethenoxydimethylolurea (cf. Specification No. 420,137) and also fatty derivatives of such bodies, for example, polyethenoxydimethylolurea stearate, polyglyceryl oleate  
75 (prepared by heating oleic acid with an excess of glycerol over that required to form the monoglyceride and an alkaline catalyst such as caustic potash: (cf. German Patent 575,911), stearyl methylglucamine polyethylene glycol ether (cf.  
80 Specification 420,518), methylglucoside polyethylene glycol ether (prepared by interaction of  $\alpha$ -methylglucoside with ethylene oxide in presence of a trace of  
85 caustic soda solution at 120—150° C.), the condensation product of monohydric alcohols such as cetyl alcohol, dodecyl alcohol, or oleyl alcohol with ethylene oxide (cf. Specification 380,431), or the  
90 condensation products of sod oil with ethylene oxide (cf. Specification 434,424). The compounds in question being neutral bodies, possessing neither acidic nor basic characteristics, are practically without  
95 effect on the affinity of the leather for dyestuffs nor do they cause any alteration of the shade normally obtained on chrome tanned leather which has been dried and wetted back. Even when employed from  
100 concentrations of about 20% (which is the optimum concentration), sweating out of the product and undesirable crystallisation within the fibre do not take place and being readily soluble in water, the use of  
105 organic solvents is unnecessary. The

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compounds are employed in aqueous solutions in the form of standing baths which are replenished as required or with agitation in a revolving drum. By this process of treatment prior to drying we obtain a clean pale green coloured leather of smooth grain readily wettable with water. The compounds we employ, having little or no affinity for the leather, are readily removed by washing with water.

The following example, in which the parts are by weight, illustrates but does not limit the invention.

EXAMPLE.

100 parts of wet chrome tanned leather from the shaving machine are immersed in a solution of 20 parts of a cane sugar-

ethylene oxide condensation product (prepared as described below) in 150 parts of water at 40° C. for 1—1½ hours. It is then dried in a chest at 40° C. when a clear greenish-white leather is obtained which on immersion in warm water wets readily and satisfactorily.

The above cane sugar ethylene oxide condensation product can be prepared by condensing 342 parts of sucrose with 1320 parts of ethylene oxide in the presence of a small amount of caustic soda under the conditions described for sorbitol in French Specification 650,973.

Dated the 25th day of October, 1935.

E. C. G. CLARKE,  
Solicitor for the Applicants.

## COMPLETE SPECIFICATION

### Improvements in the Treatment of Chrome Tanned Leather

We, JOHN BURCHILL, HENRY ALFRED PIGGOTT, and GEORGE STUART JAMES WHITE, all of Hexagon House, Blackley, Manchester, all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

Chrome tanned leather when once dried is difficult or impossible to wet back satisfactorily for dyeing purposes by simple immersion in water, whether or not accompanied by mechanical assistance such as is obtained by drumming.

Various proposals have been made for overcoming this difficulty, for instance, the chrome tanned leather, previous to drying, is treated with an aqueous solution of an aromatic sulphonic acid or its salts or of a monoacylated or unsymmetrically diacylated diamine, or, previous to drying, the leather is treated with a strong aqueous solution of a highly soluble inorganic salt such as magnesium chloride, or the leather, previous to drying, is dehydrated by treatment with acetone.

However effective any one of these processes may be, they suffer from certain disadvantages. Thus when treated with an organic base or sulphonic acid as above described, the affinity of the leather for dyestuffs as compared with non-treated (undried) leather is altered so that the leather dyer is liable to obtain on such leather with a given dyestuff results

different from those to which he is accustomed; in the case of treatment with solutions of inorganic salts the salts on drying and storage may sweat out, forming undesired incrustations and crystallising within the pores of the leather, thus subjecting it to injurious stresses and causing shrinkage. The acetone method necessitates the use of an expensive organic solvent and a special plant is necessary for its economical recovery.

We have discovered a process whereby direct chrome tanned leather may be improved and rendered amenable, after drying, to ready wetting back, and at the same time the above enumerated disadvantages avoided.

Our process consists in treating the chrome tanned leather, previous to drying, with an aqueous solution of a substantially neutral polyhydroxy compound containing at least one ether group or a polyether compound which may or may not contain free hydroxyl groups. These compounds are characterised by high water solubility.

As examples of such we mention condensation products of carbohydrates, particularly the sugars, with ethylene oxide, polyethylene oxide itself (cf. British Specification No. 346,550), the polyglycerols, condensation products of substances containing hydroxy or amido groups with ethylene oxide, for example polyethenoxyurea (cf. British Specification No. 432,356) or polyethenoxydimethylolurea (cf. British Specification No. 420,137) and also fatty derivatives of such bodies, for example, polyethenoxydimethylolurea stearate, polyglyceryl oleate (prepared by heating oleic

acid with an excess of glycerol over that required to form the monoglyceride and an alkaline catalyst such as caustic potash; (cf. German Specification No. 575,911) stearyl-methylglucamine polyethylene glycol ether (cf. British Specification No. 420,518) methylglucoside polyethylene glycol ether (prepared by interaction of  $\alpha$ -methylglucoside with ethylene oxide in presence of a trace of caustic soda solution at 120–150° C.), the condensation product of monohydric alcohols such as cetyl alcohol, dodecyl alcohol, or oleyl alcohol with ethylene oxide (cf. British Specification No. 380,431), or the condensation products of sod oil with ethylene oxide (cf. British Specification No. 434,424).

We do not include compounds such as acetals or semi-acetals which do not contain a true ether grouping. The compounds in question being neutral bodies, possessing neither marked acidic nor marked basic characteristics, are practically without effect on the affinity of the leather for dyestuffs, and they do not cause any alteration of the shade normally obtained on chrome tanned leather which has been dried and wetted back. Even when employed from concentrations of about 20%, sweating out of the product and undesirable crystallisation within the fibre do not take place and, being readily soluble in water, the use of organic solvents is unnecessary. The compounds are employed in aqueous solutions, preferably in concentrations of from 3% to 30%, in the form of standing baths which are replenished as required, or the baths may be applied with agitation in a revolving drum. By this process of treatment prior to drying we obtain a clean pale green coloured leather of smooth grain readily wettable with water. The compounds we employ, having little or no affinity for the leather, are readily removed by washing with water.

Specification No. 380,431 describes and claims the manufacture of polyethyleneglycol derivatives, and mentions generally that they may find employment, inter alia, in the leather industry. The special problem with which the present invention is concerned is not referred to.

The following examples, in which parts are by weight, illustrate but do not limit the invention.

#### EXAMPLE 1.

100 Parts of damp full chrome tanned and neutralised calf skins from the shaving machine are drummed in a solution of 20 parts of a cane sugar/ethylene oxide condensation product prepared as described below, dissolved in 150 parts water at about 40° C. for 1 to 1½ hours.

The skins are then horsed up and allowed to drain, and dried at a temperature of 35–40° C. when a clear greenish-white leather is obtained which on subsequent immersion in warm water wets readily and satisfactorily.

The above cane sugar/ethylene oxide condensation product can be prepared by condensing 342 parts of sucrose with 1320 parts of ethylene oxide in the presence of a small amount of caustic soda by heating under pressure for 12 hours at 140° C.

#### EXAMPLE 2.

100 Parts of damp shaved goat skins, chrome tanned and neutralised, are drummed in a solution containing 12 parts of polyethyleneglycol in 200 parts of water at 40° C. for 1½ to 2 hours. The skins are then horsed up, allowed to drain and finally air-dried. A leather is obtained. The polyethyleneglycol ("polyethylene oxide"; cf. Staudinger, "Die Hochmolekular Organische Verbindungen," Berlin, 1932, pp. 288–9) was prepared by interaction of 300 parts of ethylene oxide with 18 parts of ethyleneglycol in presence of a small amount of caustic soda at 100° C. in an autoclave.

#### EXAMPLE 3.

100 Parts of wet chrome tanned sheep skins, shaved and neutralised, are drummed in a solution containing 10 parts polyglycerol (prepared by heating glycerol with 1% by weight of 50% aqueous caustic potash at 280° C.) dissolved in 200 parts of water at 40° C. for 1 to 1½ hours. After horsing up the drained skins are air-dried, when a leather practically unaffected in shade is obtained, which may be stored in the dry state and wetted back in warm water when required for further treatment. Instead of polyglycerol, polyglycerol esters, for example, polyglyceryl acetate or polyglyceryl oleate may be employed. These are readily formed by esterifying polyglycerol prepared as above with the appropriate acid or acid anhydride, or in the case of the higher fatty acids, directly from glycerol and the appropriate fatty acid as described in the German Specification No. 575,911.

#### EXAMPLE 4.

100 Parts of chrome tanned hides from the shaving machine are neutralised and drummed for 2 hours at 40° C. in a solution of 15 parts of polyetheneoxyurea (prepared as described in British Specification No. 432,356. Example 2, first paragraph) dissolved in 200 parts of water. The hides are then horsed up, allowed to drain and eventually air-dried. The leather so obtained is not appreciably



effected in appearance and may readily be re-wetted as desired. In the above example there may be used instead of polyethenoxyurea an equal weight of 5 polethenoxydimethylolurea or its stearate (cf. British Specification No. 420,137) with like result.

EXAMPLE 5.

100 Parts of damp full chromed calf 10 skins from the shaving machine are neutralised and drummed in a solution of 12 parts of stearyl methylglucamine polyethylene glycol ether (cf. British Specification No. 420,518, Example 4) in 200 15 parts water for 1½ hours at 40° C. Afterwards the skins are horsed up, drained and air-dried. The resulting dry leather is readily wetted back when desired for 20 further processing by immersion in warm water. Similar results may be obtained by using instead of stearyl methylglucamine polyethyleneglycol ether in the above example an equal quantity of methyl glucoside polyethyleneglycol 25 ether.

EXAMPLE 6.

100 Parts of neutralised damp shaved chrome tanned goat skins are drummed in 200 parts of a 6.5% aqueous solution of 30 the sod oil/ethylene oxide condensation product described in Example 3 of British Specification No. 434,424. After this treatment the horsed-up and drained skins are air-dried.

EXAMPLE 7.

35 100 Parts of wet chrome tanned sheep skins from the shaving machine are first

neutralised and then immersed in 200 parts of a 6% solution of the substance sold under the trade name of Emulphor 40 O, which is presumed to have the constitution  $C_{12}H_{25}(OC_4H_9)_nOH$ , where  $n$  is greater than 10 (see Chwala, Oesterr. Chem. Ztg., 1935, No. 1, page 4) at 40°—45° C. After horsing-up, the drained 45 skins are air-dried. They may then be stored in the dry state and are readily re-wetted when desired.

Having now particularly described and ascertained the nature of our said invention 50 and in what manner the same is to be performed, we declare that what we claim is:—

1. The process of improving chrome tanned leather which comprises treating 55 the leather, previous to drying, with an aqueous solution of a substantially neutral polyhydroxy compound containing at least one ether group or a polyether compound which may or may not contain 60 free hydroxyl groups.

2. Process according to Claim 1 in which the concentration of the aqueous solution is from 3% to 30%.

3. Process for improving chrome tanned 65 leather substantially as described with reference to each of the foregoing examples.

4. Chrome tanned leather whenever treated according to the process of any of 70 Claims 1 to 3.

Dated the 26th day of October, 1936.

E. C. G. CLARKE,

Solicitor for the Applicants.